available at www.sciencedirect.com
ScienceDirect
www.elsevier.com/locate/fuproc

Review

Pyrolysis of *Pinus pinaster* in a two-stage gasifier: Influence of processing parameters and thermal cracking of tar

Wanignon Ferdinand Fassinou[a,*], *Laurent Van de Steene*[b,1], *Siaka Toure*[a,2], *Ghislaine Volle*[b,1], *Philippe Girard*[b,1]

[a] *Laboratoire d'énergie solaire-UFR-S.S.M.T. Université de Cocody, 22BP582 Abidjan 22, Côte d'Ivoire*
[b] *CIRAD-Forêt, TA 10/16, 73, avenue J.-F. Breton, 34398 Montpellier, Cedex 5, France*

ARTICLE DATA

Article history:
Received 3 December 2007
Received in revised form 22 July 2008
Accepted 26 July 2008

Keywords:
Pyrolysis
Tars
Temperature
Residence time
Kinetics
Energy evaluation

ABSTRACT

A new two-stage gasifier with fixed-bed has recently been installed on CIRAD facilities in Montpellier. The pyrolysis and the gasifier units are removable. In order to characterise the pyrolysis products before their gasification, experiments were carried out, for the first time only with the pyrolysis unit and this paper deals with the results obtained. The biomass used is *Pinus pinaster*. The parameters investigated are: temperature, residence time and biomass flow rate. It has been found that increasing temperature and residence time improve the cracking of tars, gas production and char quality (fixed carbon rate more than 90%, volatile matter rate less than 4%). The increase of biomass flow rate leads to a bad char quality.

The efficiency of tar cracking, the quality and the heating value of the charcoal and the gases, indicate that: temperature between 650 °C and 750 °C, residence time of 30 min, biomass flow rate between 10 and 15 kg/h should be the most convenient experimental conditions to get better results from the experimental device and from the biomass pyrolysis process.

The kinetic study of charcoal generation shows that the pyrolysis process, in experimental conditions, is a first-order reaction. The kinetic parameters calculated are comparable with those found by other researchers.

© 2008 Elsevier B.V. All rights reserved.

Contents

1. Introduction 76
2. Experimental 77
    2.1. Apparatus and experimental procedure 77
    2.2. Reactor temperatures 78
    2.3. Biomass feedstock and operating parameters 78
3. Results and discussion. 79

---

[*] *Corresponding author*. Tel.: +225 07 21 33 66; fax: +225 22 48 38 07.
E-mail addresses: faswaniferd@caramail.com (W.F. Fassinou), steene@cirad.fr (L. Van de Steene).
[1] Tel.: +33 4 67 61 65 22 ; fax: +33 4 67 65 15.
[2] Tel.: +225 07 21 33 66; fax: +225 22 48 38 07.

0378-3820/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2008.07.016

- 3.1. Yield of pyrolysis products . . . 79
  - 3.1.1. Influence of temperature. . . . 79
  - 3.1.2. Influence of residence time . . . 79
- 3.2. Pyrolysis charcoal . . . 80
  - 3.2.1. Influence of temperature . . . 80
  - 3.2.2. Influence of biomass flow rate . . . 80
  - 3.2.3. Influence of residence time . . . 82
- 3.3. Pyrolysis gases . . . 82
  - 3.3.1. Influence of temperature . . . 82
  - 3.3.2. Influence of residence time . . . 84
- 3.4. Pyrolysis liquid . . . 84
- 3.5. Pyrolysis products: energy evaluation . . . 85
- 3.6. Kinetic study of charcoal generation . . . 87

4. Conclusions . . . 87

Acknowledgements . . . 89

References . . . 89

Nomenclature

CNRS	Centre National de la Recherche Scientifique (National Centre of Scientific Research)
CIRAD	Centre de Coopération Internationale en Recherche Agronomique pour le développement (French Agricultural Research Centre for International Development)
E	energy of activation (cal mol^{-1} or J mol^{-1})
FC	fixed carbon (%)
HHV	high heating value (MJ/kg)
HV	heating value (MJ/kg)
K	reaction speed constant or kinetic constant (s^{-1})
Ko	pre-exponential factor (s^{-1})
R	constant of perfect gases (8.31 J mol^{-1} K^{-1})
T	selected temperature (K)
TGA	Thermogravimetric Analysis
VM	volatile matter (%)
$f=f\ (T, \mathrm{ts})$	fraction of maritime pine not converted to charcoal at time ts
$\mathrm{fo}=f\ (T, 0)$	fraction of maritime pine not converted to charcoal at initial time
$m\ (T, 0)=m_0$	mass flow rate entering (initial mass of maritime pine in kg/h)
$m\ (T, \mathrm{ts})=m$	outgoing mass flow rate (mass of charcoal in kg/h)
n	order of the reaction
t	time(s)
ts	residence time (s)
α	conversion rate of the material
ρ	density of material at the moment t (kg/m^3)
ρc	final density of the material (kg/m^3)

1. Introduction

Confronted to fossil fuels crises, renewable energies represent an alternative solution to solve the world growing energy consumption problem. New energies, in the majority of cases, have the quality to protect human environment against negative effects caused by the use of oil or “black gold”.

Biomass is one of these sources of energy whose thermochemical transformation generates gases, liquids and solid fuels. These derived products can partially replace fossil fuels [1] in order to produce heat, electricity and/or chemical products.

Among all the procedures used to transform biomass into useful products, thermochemical methods such as pyrolysis and gasification are the most appropriate and the most commercially used [1].

Today, gases resulting from the pyrolysis and/or the gasification of the biomass may be used as fuel in fuel cells. Unfortunately these gases contain a strong rate of tars which reduces their use. Therefore it is useful to revise their technique of production. Among the recommended techniques is the staged gasification where the pyrolysis process and the gasification one are carried out in different but complementary units. Hence a pilot staged gasification was installed on CIRAD facilities in Montpellier for experiments.

The maritime pine which grows well around the Mediterranean Sea is used as biomass for the experiments.

In this study, the products obtained, after a conventional pyrolysis, are analysed according to temperature, residence time and biomass flow rate. These products are gas, liquids (tars) and charcoal. Generally, temperature effect on pyroligneous products is studied. The present paper explores the effects of temperature as well as biomass flow rate and its residence time in this new kind of reactor. The results show that residence time influence must not be neglected even if temperature stays the main variable.

The main purpose of the experiments is to study the efficiency of the experimental device during a pyrolysis process. A particular stress will be laid on the thermal cracking of pyrolysis tars which is not enough investigated but also on the quality and the quantity of the charcoal and the gas produced. Kinetic and energetic studies were undertaken on these products and the results obtained are compared, if possible, with those obtained by other researchers.

2. Experimental

2.1. Apparatus and experimental procedure

The experimental device is a two-stage gasifier. It consists of two principal units: the pyrolysor and the gasifier which are separable [2].

In this paper only the experiments done with the pyrolysis unit (Fig. 1) are presented hence the apparatus description is focused on it.

Table 1 – Characteristics of each heating zone and its function

No. of the zone	Power of heating	Length of heating zone	Function of the zone
1	10.2 kW/400 V three-phase	0.98 m	Drying, torrefaction and pyrolysis beginning
2	10.2 kW/400 V three-phase	0.98 m	Pyrolysis
3	3.4 kW/230 V single-phase current	0.45 m	Pyrolysis. After this last heating zone begins the cooling zone

The pyrolysis unit consists of a steel cylinder provided with a heating system. The cylinder is horizontal and crossed by an endless screw which leads the raw material from its entrance to its exit.

In the lower part of the reactor's exit, a barrel collects the charcoal while at its top, the off gas is drained to the post-combustion chamber.

The experimental device is commanded by two automatic systems: the first is intended to programme automatically the biomass flow to be pyrolysed and its residence time in the reactor. The second commands the heating system.

The heating system is composed of a series of heating resistances which surround the pyrolysor cylinder. They are gathered in three zones. The temperature of each zone can be programmed independently of that of the others.

All experiments were carried out isothermally in a slow pyrolysis regime.

In the experiments, the variables are: the biomass flow rate, the temperature and the residence time.

The biomass used is the maritime pine wood chips. No gas carrier is used for the experiments.

To begin an experiment, the heating system is put on and the experimental temperature is fixed. When the reactor reaches a steady regime, the biomass flow and its residence

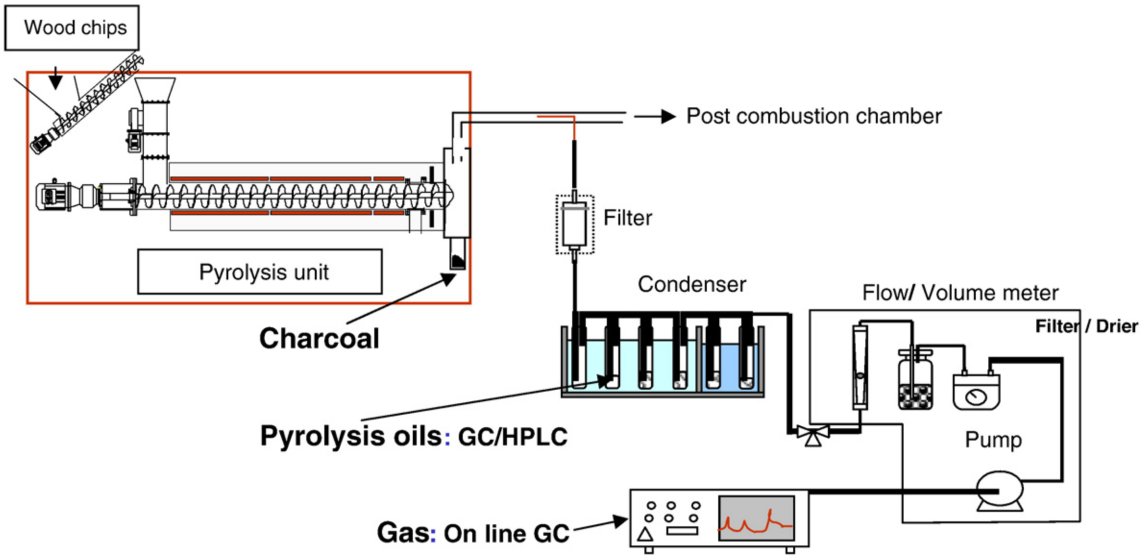

Fig. 1 – Experimental device.

time are programmed. Then the experiment starts by the introduction of the raw material into the unit.

The system is built to work continuously until the exhaustion of the stock of biomass.

During the experiment progress, samples of the off gas are continuously taken, condensed; the non-condensable fraction of this gas is analysed on line by a gas chromatograph (Micro-GC Bench CP-2003) connected to a computer. The non-condensable fraction is composed mainly of H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, N_2,… At the end of an experiment, the quantities of charcoal, gas and liquid collected are measured and their samples are later analysed. Ultimate analysis of the wood chips is done in the laboratories of CNRS at Vernaison (France) while all the others are done in CIRAD laboratories at Montpellier (France) by using French norm: NB 55-101 [3] and tar protocol [4,5].

2.2. Reactor temperatures

The reactor is approximately 3 m long. So from the entrance to the exit of the pyrolysis cylinder, it is difficult to maintain a constant temperature because of heat transfer effects, thermochemical process and edge effects.

To minimise the previous phenomena, the pyrolysis cylinder is divided into three areas: their characteristics and functions are summarised in Table 1. Ten thermocouples (K type) fixed along the cylinder of the reactor, allow getting temperature profiles during pyrolysis process. Different curves (Fig. 2) show that the set point temperatures are generally respected in the second and the third zones. The set point temperatures are 450 °C, 550 °C, 650 °C and 750 °C for various flows of wood chips and residence times. These observances confirm the good design of the heating system and its good insulation (Fig. 2).

The temperature profiles of Fig. 2 can be explained as follows. Before entering the pyrolysis unit, the biomass is at ambient temperature. During a short transient period, its temperature increases until reaching that of the pyrolysor. This sudden thermochemical process needs an important quantity of energy which makes the reactor's temperature at the entrance decrease. While crossing the reactor, the temperature of the biomass rises, reaches its upper value and then starts to drop while moving towards the exit of the cylinder. These phenomena explain why temperature profiles are not straight lines but curves.

2.3. Biomass feedstock and operating parameters

The biomass used was pine wood chips delivered from Ardeche (France). Its scientific name is *Pinus pinaster* (Alton, 1789) and it belongs to Pinacea family.

The experiments, with this raw material on the pilot, were carried out by varying the biomass flow rate (10, 15, 20 kg/h), the residence time (15, 30, 60 min) and the temperature (450 °C, 550 °C, 650 °C, 750 °C).

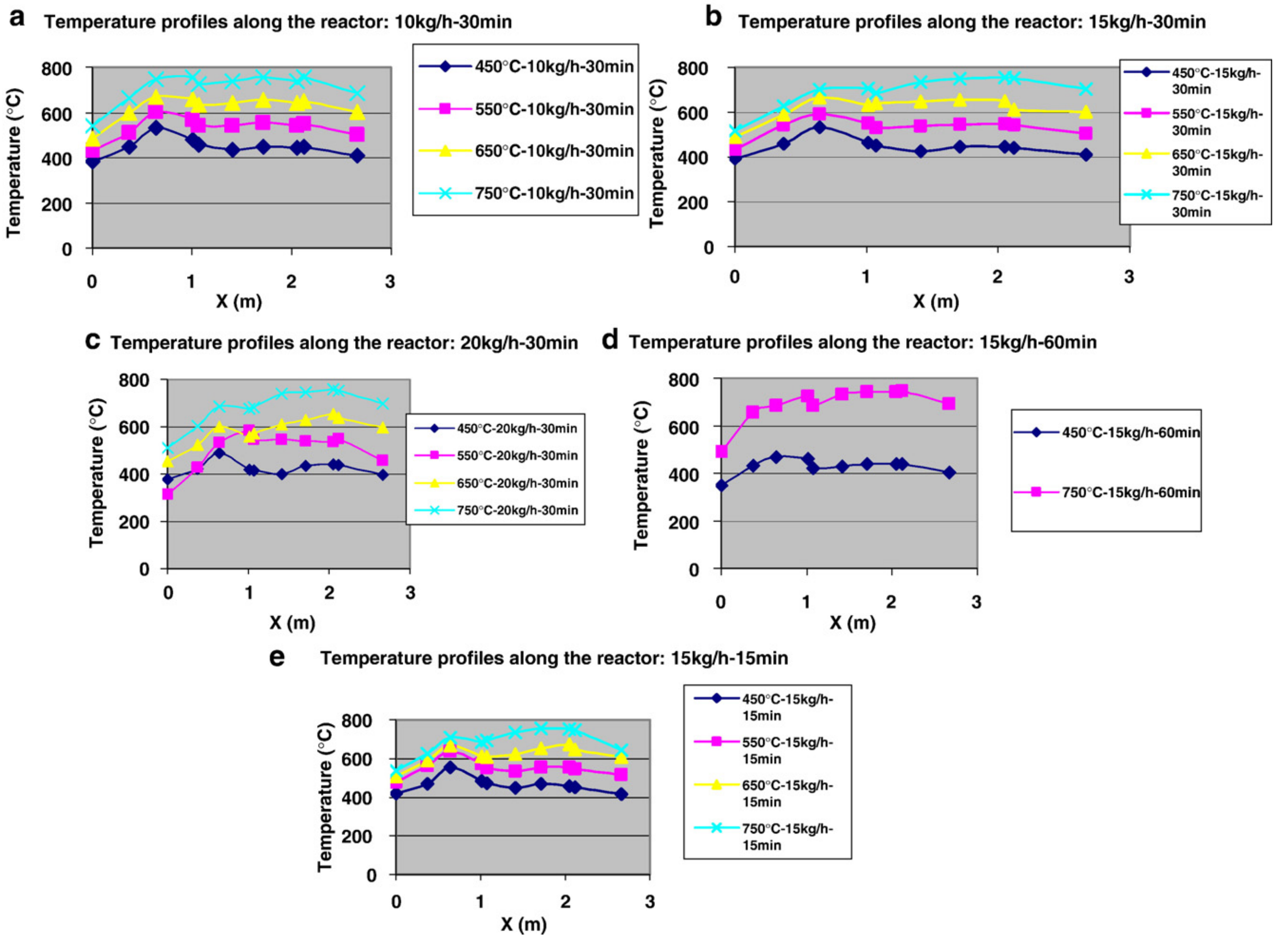

Fig. 2 – Temperature profiles along the reactor for different biomass flow rates and residence times.

Table 2 – Pine wood chips characteristics

	Percentage
Proximate analysis (on dry basis)	
Moisture content	15%
Volatile matter rate	81.3%
Fixed carbon	18.5%
Ashes rate	0.2%
High heating value	19.3 MJ/kg
Ultimate analysis (on dry basis)	
C	45.28%
H	5.68%
O	42.75%
N	<0.30%
S	<0.10%
Granulometry (average)	
Length	30 mm
Width	15 mm
Thickness	5 mm

Some previous works have reported that reduced particle size below 5 mm does not exert any influence on the pyrolysis process and the yield of its products [6,7]. They have shown that a high particle size limits heat transfers between the surface and the inside of the particle. According to the kind of pyrolysis unit (here screw pyrolysis unit), appropriate size must be chosen to improve pyrolysis/gasification reactions and the motions of the particles. These considerations led to the choice of the particle size given in Table 2. This size also complies with the regulation existing in France for wood boilers. For the experiments, it is taken mainly into account the fact that after the pyrolysis process, the charcoal obtained will be gasified in a fixed-bed reactor whose inner diameter is 200 mm. So if the particle size is too small, it causes the problem of stability of the bed.

3. Results and discussion

3.1. *Yield of pyrolysis products*

3.1.1. *Influence of temperature*

Table 3 gives data on charcoal, liquid and gas production for the following variables: biomass flow rate, residence time and temperature.

For fixed residence time and biomass flow, the fractions of charcoal and liquid decrease when the percentage of gas rises while temperature increases.

At 450 °C, for the same residence time, biomass flow rate has no influence on the gases production. At reverse, for the same biomass flow rate, the percentage of the gases increases with the growth of residence time.

For 450, 550 and 650 °C, the percentage of liquid is, generally, higher than both that of gas and charcoal except some particularities.

At 750 °C, the gas yield is more important than that of the liquid and the charcoal. So for this temperature, the classification for the pyrolysis products is, in decreasing order: gas, liquid and charcoal.

The explanation of this result can be found in literature [1,10]. It is reported that the reactions of thermal cracking, decarboxylation and depolymerization are favored by the rise of temperature and consequently highly increase the gas produced percentage. It can thus be concluded that low temperatures support the production of charcoal and liquid while high temperatures that of gases. An increase in temperature leads to the transformation of volatile and organic matters and other hydrocarbons in gas [9].

The previous analyses do not concern the experiment carried out for 20 kg/h: its result is put in Table 3 to analyse the influence of biomass flow rate (Section 3.2.2).

3.1.2. *Influence of residence time*

From Table 3 the increase of charcoal yield with residence time can be seen. When residence time is 15, 30 or 60 min, its influence on liquid and gas production is not generally remarkable. At 450 °C however an appreciable increase of gas production appears when the residence is increased.

Lots of complex phenomena (thermal and chemical reactions) happen during a pyrolysis process when residence time increases. Consequently, it is difficult to get general laws for gas and liquid yield, except for charcoal. It is logical to think that increasing temperature and residence time promote liquid or tar cracking, which increases gas percentage that has been produced [7]. Temperature seems to influence this temporary variable strongly. More investigations must be made to get better results and explanations.

The increase of charcoal percentage with the rise of residence time (except at 450 °C) can be explained by the fact

Table 3 – Yield of pyrolysis products (wt.%) versus temperature

Temperature (°C)	10 kg/h–30 min			15 kg/h–15 min			15 kg/h–30 min			15 kg/h–60 min			20 kg/h–30 min
	Char	Liquid	Gas	Char	Liquid	Gas	Char	Liquid	Gas	Char	Liquid	Gas	Char
450	31.94	49.86	18.21	35.30	50.34	14.36	30.55	51.28	18.17	32.56	45.82	21.62	32.73
550	23.08	48.67	28.25	23.46	51.63	24.91	26.22	50.56	23.22	–	–	–	24.08
650	19.55	32.70	47.75	18.77	43.80	37.43	19.76	42.32	37.93	–	–	–	20.85
750	17.73	25.78	56.49	16.77	30.38	52.85	17.87	22.91	59.22	20.35	31.73	47.92	18.25

Table 4 – Proximate analysis of charcoal on dry basis (wt.%)

Temperature (°C)	10 kg/h–30 min			15 kg/h–15 min			15 kg/h–30 min			15 kg/h–60 min			20 kg/h–30 min		
	VM	FC	Ash	VM	FC	Ash	VM	FC	Ash	VM	FC	Ash	VM	FC	Ash
450	28.5	70.45	1.05	34.70	64.05	1.25	30.07	68.97	0.93	25.20	73.80	1.00	36.00	62.70	1.34
550	16.73	81.90	1.40	19.45	79.15	1.40	20.15	78.70	1.20	15.10	83.90	1.00	18.20	80.55	1.23
650	7.40	91.25	1.35	9.60	88.75	1.66	8.10	90.70	1.20	8.20	90.80	1.00	9.75	88.60	1.46
750	4.50	94.00	1.49	4.55	93.90	1.55	3.85	94.70	1.45	3.10	95.50	1.35	4.00	94.35	1.67

that increasing residence time obliges hot charcoal to be exposed to pyrolysis vapours for a long time. It should be remembered that pyrolysis process is continuous here: so fresh biomass enters the reactor and its vapours encounters the “old and hot” charcoal previously pyrolysed. The hotter the charcoal is, the higher its affinity to absorb the vapours of pyrolysis is. Thus, high temperatures combined with great residence times in the reactor lead to a heavy charcoal. In the same way, a small residence time combined with low temperature, also leads to a heavy charcoal because the process of pyrolysis does not have sufficient time to proceed. Heat transfers are also limited. Consequently, the charcoal obtained is full of humidity and VM; its mass percentage is also high. The influence of the experimental parameters on the composition of the pyroligneous liquids, the production and the quality of charcoal as well as the production of gas will follow the general study of the pyrolysis products.

3.2. *Pyrolysis charcoal*

3.2.1. *Influence of temperature*

For all biomass flow rates (10 kg/h, 15 kg/h, 20 kg/h), residence times (15, 30, 60 min) and according to Table 4, an increase of temperature leads to a decrease of VM rate and an increase of FC rate.

The rate of ash yield increases slowly between 1 and 1.7 with the evolution of temperature in general. Thus, in experimental conditions, ash fraction increases from 20 to 30% when temperature varies from 450 to 750 °C.

Some explanations of the previous observations can be the following: the molecules which constitute biomass crack when they are submitted to thermal effect, and particularly when they are light. It is known that increasing temperature strengthens this phenomenon and can explain the behaviour of the rate of VM previously observed. So the decrease of VM with temperature leads to an increase of FC rate and thus the production of first rate charcoal.

When temperature reaches 650 °C and 750 °C, the charcoal obtained has greater quality (rate of FC > 90%) according to French specifications (AFNOR, 1984) [3] and can be used in metallurgical, chemical, pharmaceutical and food industries [8,9].

It should be noted that, the charcoal quantity produced decreases when pyrolysis process temperature rises (Table 3): so the quality and quantity of charcoal move in reverse direction with temperature (Tables 3 and 4). The decrease of charcoal yield is due to the fact that increasing temperature improves charcoal quality by reducing its mass and VM, but increases FC.

The results obtained here show the remarkable influence of temperature on the quality and the quantity of charcoal in pyrolysis process. They also comply with those obtained by other researchers [1,6,8,9] although the raw materials are not always the same.

3.2.2. *Influence of biomass flow rate*

For this study (Tables 3 and 4), residence time is fixed and the biomass flow rates are 10 kg/h, 15 kg/h and 20 kg/h. The quality and the quantity of the charcoal are analysed for the following temperatures: 450 °C, 550 °C, 650 °C and 750 °C.

Generally, for most temperatures (except at 450 °C) and for a fixed residence time of 30 min, the charcoal yield for 10 kg/h, is lower than that obtained at 15 kg/h and 20 kg/h (Table 3). This phenomenon can be explained by the fact that with a low biomass flow rate, heat exchanges and transfers in biomass are better. So water and VM contained in the raw biomass are easily ejected. The consequences of this fact are: the reduction of VM's rate, the decrease of the charcoal efficiency, and the increase of FC's rate with the decrease of biomass flow rate (Table 4).

Hence, it can be concluded that charcoal quality for low biomass flow rate (10 kg/h) is generally better than the one obtained at high flow rates.

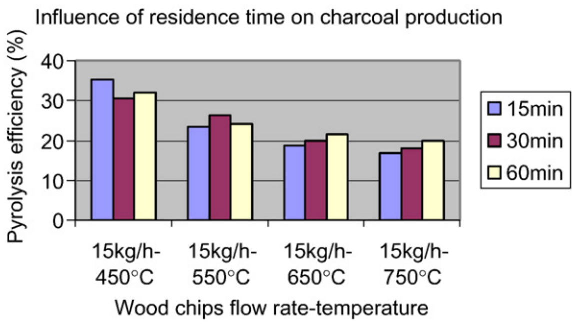

Fig. 3 – Influence of residence time on charcoal production at fixed biomass flow rate: 15 kg/h.

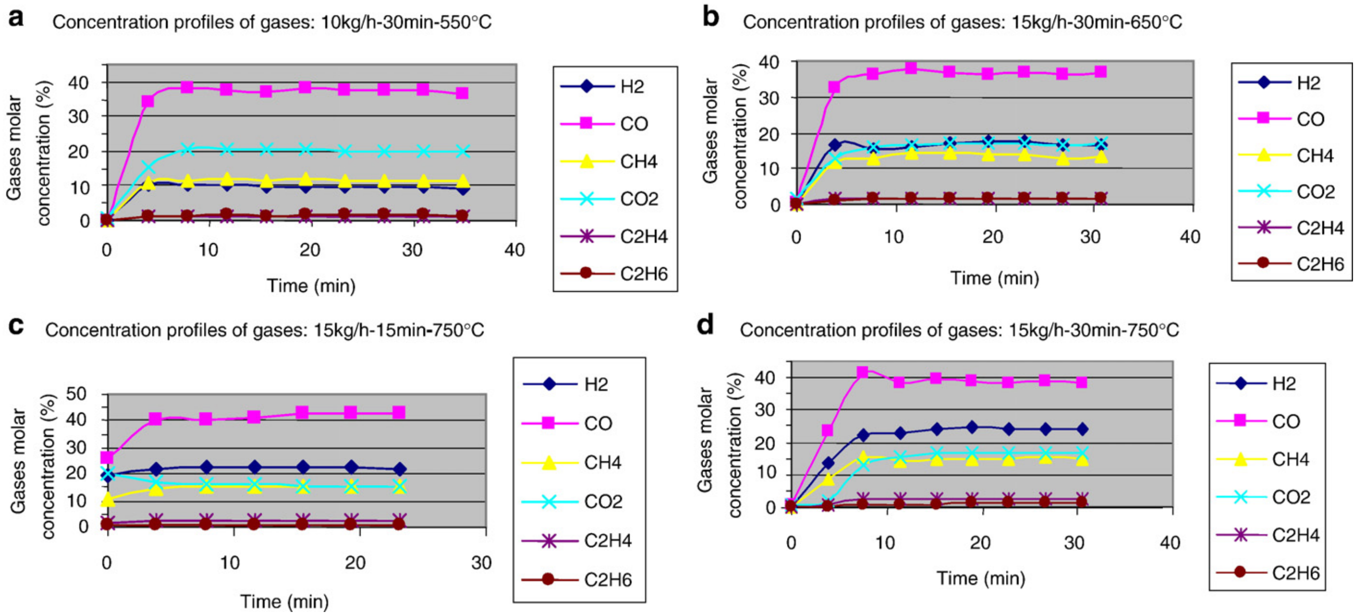

Fig. 4 – Concentration profiles of gases produced at different biomass flow rates and temperatures for a fixed residence times.

It is remarkable that at 750 °C, varying biomass flow rate causes weak differences on the charcoal parameters studied (MV, FC, ashes, pyrolysis efficiency).

3.2.3. *Influence of residence time*

For this study, biomass flow rate is fixed to 15 kg/h. The analysis of the result is made for three residence times: 15, 30 and 60 min at different temperatures (Table 4).

At higher temperatures (650 °C and 750 °C), the yield of charcoal increases when residence time goes up (Table 3); it is the contrary at 450 °C. This phenomenon can be explained by the fact that staying for a long time in the reactor and at high temperatures, increases charcoal's affinity to absorb vapours caused by pyrolysis process and the drying of fresh biomass.

This reaction depends strongly on the level of temperature: so this fact is not observed at low temperatures (450 °C and 550 °C) for the same residence times. It is noticed that charcoal rates at 650 °C and 750 °C are lower than those obtained at 450 °C and 550 °C. At this last temperature (550 °C), residence time effects are difficult to be appreciated (Fig. 3). All these results show that increasing residence time leads to the improvement of the quality of the charcoal: VM decreases while FC's rate goes up. As matter of fact, high residence time improves heat exchanges and the transfers of heat in biomass during the pyrolysis process; thus VM and other molecules are easily cracked. Consequently, FC rate increases and the quality of charcoal is improved. It should be noted that the rate of ash yield decreases when residence time evolves but slowly.

3.3. *Pyrolysis gases*

The main gases which appear during the pyrolysis process are H_2, CO, CH_4, CO_2 and some low molecular weight hydrocarbons such as ethane (C_2H_6), ethylene (C_2H_4). In some cases oxygen (O_2) and nitrogen (N_2) are also detected and they are introduced in Table 9 to show the performances of the experimental set-up and the pyrolysis process. These last two gases can result from biomass decomposition and/or the absorbed air [7] but it should be noted that nitrogen is not used as gas carrier for the experiments.

Fig. 4 shows the concentration profiles of H_2, CO, CH_4, CO_2, C_2H_4, and C_2H_6 according to time for different experimental conditions:

- biomass flow rates: 10 and 15 kg/h
- temperature: 550 °C, 650 °C and 750 °C
- residence time: 30 and 15 min.

As it can be seen (Fig. 4), the trend of the curves is similar for all experiments. Generally, around 10 min after the beginning of the pyrolysis process, the gases reach their maximum concentration which remains at the same level until the exhaustion of the raw material. CO has the highest molar concentration while C_2H_4 and C_2H_6 the lowest, independently of the experimental conditions; but that of H_2, CO_2 or CH_4 depends on them.

3.3.1. *Influence of temperature*

For all biomass flow rates and residence times, the rate of H_2, CO, CH_4, CO_2, C_2H_4 or C_2H_6 increases with the rise of temperature as shown in Table 5.

Under the experimental conditions, the highest temperatures lead to high gas rates. Consequently, the gas production also evolves in the same direction as the temperature.

The main explanation is due to the thermal cracking of all molecules contained in the biomass. It is known that this phenomenon is strongly influenced by the rise of temperature during the pyrolysis process [1,7]: so that the higher the temperature, the higher the production of each component of the pyrolysis gas is. The classification in decreasing order is: CO, H_2, CO_2, CH_4 and C_2H_6 according to

Table 5 – Gas production (kg of gas/kg of pine wood chips) *10^3: temperature effect

Temperature (°C)	10 kg/h–30 min								15 kg/h–15 min							
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	O_2	N_2	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	O_2	N_2
450	0.31	54.74	7.15	82.21	0.90	1.39	0.00	35.30	0.64	61.90	21.62	43.63	0.93	1.41	0.00	13.20
550	1.93	115.41	20.15	96.12	2.85	4.68	0.52	41.33	1.45	101.45	91.84	17.08	2.63	3.44	0.00	31.44
650	7.32	203.27	43.07	132.15	9.32	10.38	0.00	72.46	5.08	181.96	33.34	109.75	7.11	7.09	0.00	30.33
750	14.07	245.33	62.51	172.09	13.31	6.58	0.00	51.10	9.56	275.22	53.38	138.85	15.26	6.55	0.00	29.85

Temperature (°C)	15 kg/h–30 min							
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	O_2	N_2
450	0.14	37.79	4.49	71.28	0.74	0.97	0.00	66.60
550	1.40	92.97	16.79	89.85	2.11	3.39	0.00	25.48
650	5.80	173.62	36.05	122.13	7.00	7.06	0.00	27.67
750	12.69	280.30	62.78	182.47	15.44	7.37	0.00	30.98

Temperature(°C)	15 kg/h–60 min										
	H_2	CO	CH_4	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	O_2	N_2
450	0.14	37.79	4.49	0.40	62.94	9.92	125.71	1.16	2.37	0.00	13.50
550	1.40	92.97	16.79	–	–	–	–	–	–	–	–
650	5.80	173.62	36.05	–	–	–	–	–	–	–	–
750	12.69	280.30	62.78	13.36	207.11	58.09	168.79	12.12	6.59	0.00	13.27

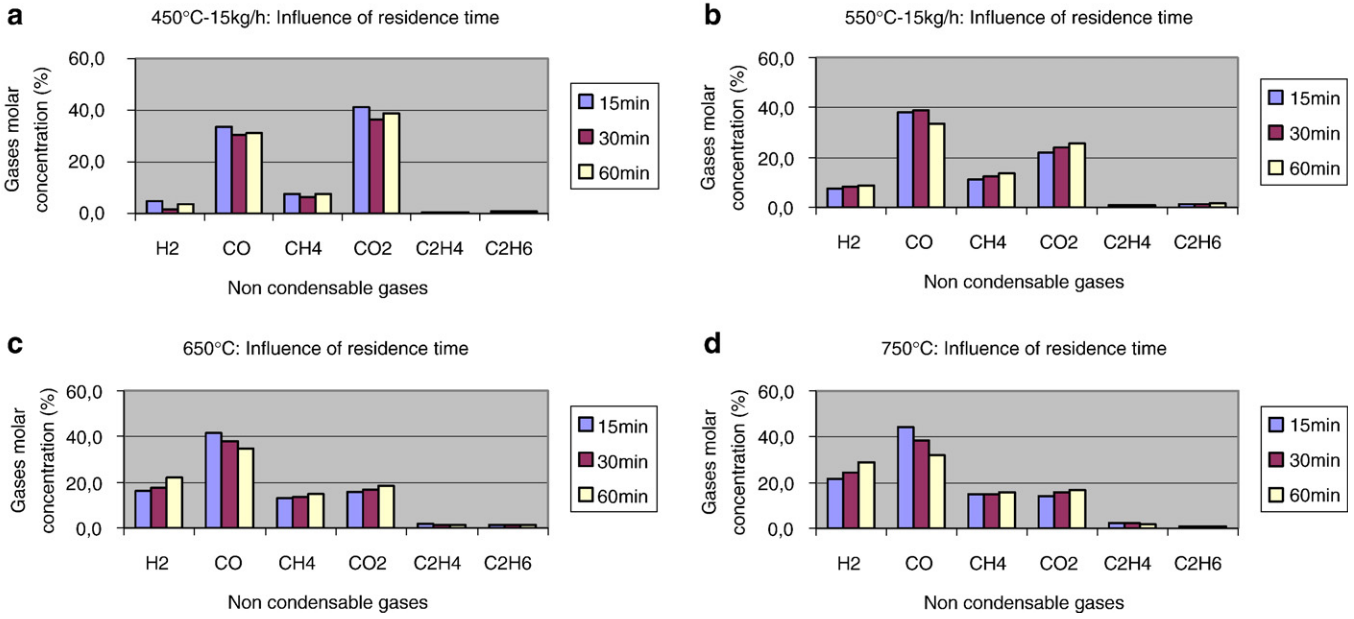

Fig. 5 – Residence time effect on gases concentration produced at different temperatures for a biomass flow rate of 15 kg/h.

the molar flows deduced from Table 5 (this classification is different when the flow of gaseous as kg/kg pinewood is considered as in Table 5). The reactions of decarboxylation, depolymerization and thermal cracking are strongly favored by the rise of temperature. Each type of these reactions supports the production of a kind of gas. Thus hydrogen and methane are formed starting from the reactions of depolymerization and the cracking of the VM whereas CO and CO_2 come from the reactions of decarboxylation and depolymerization [1,10].

3.3.2. *Influence of residence time*

For this study, the biomass flow rate is fixed to 15 kg/h. At a given temperature, the concentration of the pyrolysis gas versus the residence time is studied. The gas yield variation with residence time at 550 °C, 650 °C and 750 °C, is more remarkable than at 450 °C when it seems random. Hence all the analysis will be focused on the first three temperatures (Fig. 5).

The increase of residence time generally leads to the increase of H_2, CH_4, CO_2 and the decrease of CO; while C_2H_4 and C_2H_6 are very weakly influenced. The highest concentration of H_2, CH_4 or CO_2 is obtained at 60 min whereas this residence time corresponds to the weakest CO concentration. These phenomena are very marked at 650 °C and 750 °C.

When the residence time of the charcoal in the pyrolysis reactor increases, the reactions of cracking, depolymerization and decarboxylation have enough time to be carried out. Thus, the productions of the more share of gases increases. But CO reduction can be due to secondary reactions such as [11]:

$$\text{methanation reaction}: CO + 3H_2 \rightarrow CH_4 + H_2O \tag{1}$$

$$\text{water–gas shift reaction (a gasification reaction)}: CO + H_2O \rightarrow CO_2 + H_2. \tag{2}$$

It can be supposed that the reactions of the cracking of tars and the gasification of the carbon by the steam are supported by long residence times. Thus the following reactions of gasification can appear:

$$\text{water gas : primary} \quad C + H_2O \rightarrow CO + H_2 \tag{3}$$

$$\text{: secondary} \quad C + 2H_2O \rightarrow CO_2 + 2H_2 \tag{4}$$

$$\text{hydro gasification :} \quad C + 2H_2 \rightarrow CH_4 \tag{5}$$

$$\text{water–gas shift :} \quad CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

$$\text{steam} - \text{reforming :} \quad CH_4 + H_2O \rightarrow CO + 3H_2. \tag{7}$$

The rise of the temperature improves these reactions: that confirms the experimental results obtained at 650 °C and 750 °C.

3.4. *Pyrolysis liquid*

Table 6 gives the composition of the pyrolysis liquid according to temperature for a fixed biomass flow rate (15 kg/h) and a residence time of 30 min. The major liquid products identified in the pyrolysis liquid are, put aside the water, acetic acid, methanol, acetaldehyde, pentanal, furfural, phenol, cresol(*O*, *M*,*P*), benzene, toluene, naphthalene, and catechol. Small quantities of other components are also formed such as levoglucosan, acenaphthene, fluoren, maltol, butandion, 2-methylcyclopenten-1-one, 2-hydroxy-1-methyl-1-cyclopenten 3-one… (see Table 6 for the complete list). As shown in Table 6, liquid composition depends strongly on temperature. For example at 450 °C and 550 °C the main components are: levoglucosan, acetic acid, methanol, pentanal, furfural, catechol… but for 650 °C and 750 °C, they are: acetone, 2–3 butandion, pentanal, methanol, phenol, benzene, toluene, indene… The highest experimental temperature 750 °C has a special composition: after the light compounds like acetone, 2–3 butandion, methanol, phenol…; the stable and heavy molecules such as: benzene, toluene, naphthalene, and indene appear. Considering the family of tars, it is remarkable that light compounds like furfurals, sugar, methoxyphenols and phenolics are in the majority at low temperature (450 or 550 °C). They belong to the primary class or the secondary class of tars according to Milne et al.'s tars classification [13].

When temperature rises, the tars which belong to the family of nitrogen, benzene and aromatics, that is, secondary and tertiary tars compounds [13], become more and more important in spite of the presence of the other families tars and their small quantity.

The rise of the temperature destroys the unstable molecules whereas it supports the formation of the stable molecules. This phenomenon is much accentuated at the high temperatures (here 750 °C) although one observes the presence of some primary or secondary tars. This behaviour could be due to the cracking of liquid phase with increasing temperature [7]. The complexity of the reactions of decomposition and recombination of some molecules under the effect of the heat would also be at the base of this paradox.

These experimental results comply with those of some researchers. Morf et al. [11] reported that, according to Egsgaard and Larsen [15], guaiacol (primary tar class) is the important precursor of the formation of aromatic aldehydes (secondary tar compounds) while phenolics (secondary tar compounds) derive from the compounds of PAH. PAH compounds, particularly naphthalene, are tertiary tar compounds. According to some authors [16], benzene which is the precursor of PAH formation, decomposes by forming acetylene, when the reactions evolve.

All these examples show why during the analysis of the pyrolysis oils, some compounds appear while others disappear under temperature or residence time effects (Table 6).

It should be noted that phenolics are suspected to cause corrosion in IC engines [17] while benzene and other PAH compounds are known as highly cancerogeneous substances [11]. The conclusion of this study on the liquid of pyrolysis is as follows. The low temperatures of pyrolysis lead to a great quantity of liquids (Section 3.1) with light tars while the high temperatures reduce its production and support the heavy and stable tars which are difficult to be destroyed in the biogas and constitute the main brake of the use of the green gas in engines and/or fuel cells [14].

Table 6 – Pyrolysis liquid composition (experimental conditions: biomass flow rate = 15 kg/h–residence time = 30mn)

Family	Tar's class [12]	Compound (mg/g)	450 °C/ 30 min	550 °C/ 30 min	650 °C/ 30 min	750 °C/ 30 min	750 °C/ 60 min
Light compound		Acetic acid	16.72	15.71	6.78		
Light compound		Acetol			8.03		
Light compound	1	Acetaldehyde	2.21	7.12	16.77		
Light compound		Methanol	12.44	11.30		13.27	10.07
Light compound		Pentanal	9.03	12.65	12.31		
Light compound		2–3-Butandion			13.17	15.75	
Light compound		Acetone	2.51	6.54	19.49	45.21	17.99
Furfurals	1	Furfural	7.96	6.40	4.95		
Furfurals		2-Methylcyclopenten-1- one	1.20	1.33	1.41		
Furfurals		2-Hydroxy-1-methyl-1-cyclopenten-3-one	3.00	1.19			
Furfurals		3-Methyl-2-cyclopentenone	0.66	0.64			
Furfurals		Furfurylic alcohol		0.56	2.34		
Furfurals		5-Methyl-2-furfuraldehyde	2.03	1.39			
Furfurals		2-Acethylfuran	0.75	0.76	0.40		
Sugar	1	Levoglucosan	33.57	34.46			
Methoxyphenols	1	Guaiacol	4.35				
Methoxyphenols		Eugenol	0.89				
Methoxyphenols		4-Methyl Guaiacol	6.74				
Methoxyphenols	1	Isoeugenol trans	2.78				
Methoxyphenols		Vaniline	2.00				
Phenolics	2	Phenol	0.75	2.51	8.12	12.81	11.98
Phenolics	2	P-Cresol	0.71	1.19	2.38	0.75	1.14
Phenolics	2	M-Cresol	0.64	1.89	3.46	3.41	3.48
Phenolics	2	O-Cresol	1.00	2.26	4.56	2.58	2.88
Phenolics		2–4 Dimethylphenol	0.87	2.25	3.04		0.82
Phenolics		3,4-Dimethylphenol	0.67	1.00	0.87		
Phenolics		Maltol	1.24	2.12	1.49		
Nitrogen		3-Picolin			1.76	1.44	
Benzene	3	O-Xylen	0.27				
Benzene	4	Benzene		0.80	7.67	52.67	36.96
Benzene	3	Toluene		2.10	7.58	25.10	18.75
Benzene	3	Indene	1.05	0.79	1.55	7.24	5.62
Benzene		Catechol	3.79	6.15	3.23		
Aromatics	3	Fluoren				1.02	1.02
Aromatics	4	Phenantren				1.83	
Aromatics		Acenaphthene				0.38	0.53
Aromatics	4	Naphthalene			0.90	9.37	7.20
		Total organics (mg/g)	119.82	123.10	132.25	192.82	118.44
		Total organics (%)	11.98	12.31	13.22	19.28	11.84
		Water (%)	51.00	51.83	65.14	86.9	81.52
		Total (%)	62.98	64.14	78.36	106.18	93.36

Influence of temperature and residence time.

3.5. *Pyrolysis products: energy evaluation*

To study the energetic aspect of the products of pyrolysis, the results obtained for a flow of biomass of 15 kg/h and a residence time of 30 min which seem to be the optimum operating conditions of the pyrolysor, are analysed. The pyrolysis oils are composed of many chemicals which are likely (or already) to be used in chemical industry but their field of application can also

Table 7 – Heating values of charcoal and gases versus temperature (biomass flow rate: 15 kg/h, residence time: 30 min)

Temperature (°C)	Proximate analysis of charcoal (wt.%)			HHV charcoal		HHV gases		HHV charcoal + gases
	VM (%)	FC (%)	Ashes (%)	MJ/kg charcoal	MJ/kg pine wood	MJ/ Nm^3	MJ/kg pine wood	Total MJ/kg pine wood
450	30.07	68.97	0.93	29.11	8.89	7.38	0.74	9.63
550	20.15	78.70	1.20	30.46	7.99	12.36	2.36	10.35
650	8.10	90.70	1.20	33.64	6.65	14.43	5.31	11.96
750	3.85	94.70	1.45	32.58	5.82	15.87	9.30	15.12

HHV: high heating value.

Table 8 – Heating values of *Cynara cardunculus* L. versus temperature obtained by Encinar et al. [1]

Temperature (°C)	Proximate analysis of charcoal (wt.%)			HV* charcoal		HV* gases		HV* charcoal + gases
	VM (%)	FC (%)	Ashes (%)	MJ/kg of charcoal	MJ/kg of *Cynara*	MJ/ Nm^3	MJ/kg of *Cynara*	Total (MJ/kg of *Cynara*)
300	49.33	41.69	8.98	17.4	7.08	6.49	0.66	7.74
400	25.50	60.39	14.12	26.3	6.65	6.91	0.80	7.45
500	19.65	65.15	15.20	28.6	6.53	8.21	1.08	7.61
600	15.46	68.37	16.16	30.1	6.20	11.1	2.15	8.35
700	12.45	71.08	16.47	31.4	5.95	12.57	3.79	9.74
800	9.46	72.38	18.16	32.0	6.00	12.71	4.33	10.33

extend from the production of liquid or gaseous fuels to synthesis gases. It is a field in full exploration! Also the analyses will primarily be focused primarily on the charcoal and gases of pyrolysis for which the calorific values were calculated. In Table 7, the calorific value of gases increases with temperature in accordance with the production of the various gases which make it up: H_2, CO, CH_4, C_2H_4, and C_2H_6. The production of these gases evolves in the same direction as the temperature. The gas obtained can be classified as a gas with average calorific value since its high calorific value varies from 7 to 16 MJ/Nm^3 [18]: that is extremely appreciable for a normal pyrolysis of biomass without gasification in due form. As already shown in Section 3.2.1, the FC rate increases with temperature and thus will result in an increase in the calorific value of charcoal as illustrated in Table 7. On the other hand this calorific value decreases with temperature when it is brought back to the kilogram of biomass (maritime pine) because of the fall of the output of pyrolysis. This output evolves in the opposite direction of the temperature just as the production of the charcoal. It should be noted that the sum of the calorific values of gas and charcoal per unit of biomass is an increasing function of the temperature: that results from the previous explanations.

According to French standards: NF B 55-101, 1984 [3], a house charcoal having a minimal content of FC of (82 ± 2) % mass is a class A one. As for the class B charcoal, it has (75 ± 2) % of FC. This standard thus makes it possible to classify the charcoals produced at 650 °C and 750 °C in class A and those produced at 450 °C and 550 °C in class B although those produced at 550 °C can belong to class A or B.

Antal et al. [8] bind the quality and the use of a charcoal to its rates of VM and ashes. According to these researchers, a charcoal having a rate of VM which varies between 20 and 30% (even more 40%) can be used for domestic cooking whereas the charcoals intended for metallurgical industry must have a rate of VM from 10 to 15% (or less). Still according to these authors, a good charcoal has a rate of ashes which typically varies between 0.5 and 5%; its calorific value ranges between 28 and 33 MJ/kg. It thus clearly appears that the charcoals produced between 450 °C and 550 °C can be intended for domestic uses and those of 650 °C and 750 °C to industrial uses; however all these charcoals would be of good quality as for the ash content and the heating value.

These results show that the experimental device, although in a pilot state, is well dimensioned and makes it possible to obtain products whose qualities are comparable (and sometimes of better quality) with those produced on a small scale in laboratories [1,9]. Thus in Tables 8 and 9, the results obtained by other researchers at laboratory scale on *Cynara cardunculus* L. which is a Mediterranean seedling [1] like the maritime pine studied in this paper, and also on the bagasses of olive and grape [9] are given on a comparative basis. It can be seen that *Cynara* and maritime pine have the same behaviour according to temperature but *P. pinaster* heating values are generally higher than those of *Cynara*. The main difference between the previous biomasses and bagasses stays at the level of the sum of calorific values (charcoal and gases): that of the maritime seedlings increases with the temperature whereas that of the bagasses evolves in contrary direction.

Table 9 – Heating values of olive and grape bagasse versus temperature obtained by Encinar et al. [9]

	Olive bagasse				Grape bagasse			
	HV* charcoal		HV* gases	HV* charcoal + gases	HV* charcoal		HV* gases	HV* charcoal + gases
Temperature (°C)	MJ/kg charcoal	MJ/kg olive bagasse	MJ/kg olive bagasse	Total MJ/kg olive bagasse	MJ/kg charcoal	MJ/kg grape bagasse	MJ/kg grape bagasse	Total MJ/kg grape bagasse
300	23.21	18.11	0.05	18.16	24.73	20.36	0.04	20.40
400	25.92	12.83	0.21	13.04	29.49	16.87	0.16	17.03
500	28.08	10.14	0.35	10.49	30.31	13.43	0.34	13.77
600	31.18	10.01	0.79	10.80	30.76	12.46	0.63	13.09
700	31.71	9.96	1.17	11.13	30.05	10.88	1.17	12.05
800	31.87	9.69	1.59	11.28	32.27	10.94	1.69	12.63
900	32.72	9.49	1.78	11.27	33.27	10.78	1.95	12.73

HV: heating value.
HV*: high or low heating value not specified.

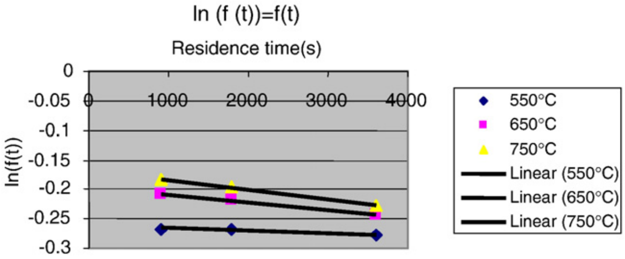

Fig. 6 – Determination of the kinetic constants *K*: curve ln (*f*)=*f* (ts): Graphically one gets: $Y_{550\ °C}=-4E-06ts-0.2634$ $R^2=0.9699$, $Y_{650\ °C}=-1E-05ts-0.1957$ $R^2=0.9968$, $Y_{750\ °C}=-2E-05ts-0.1687$ $R^2=0.9984$.

3.6. *Kinetic study of charcoal generation*

The classical equation below is often used for the kinetic interpretation of the thermal decomposition of wood and its components [19]:

$$(\partial\rho/\partial t) = -K(\rho - \rho c)^n \tag{8}$$

$$K = \mathrm{Ko}^{*}\mathrm{Exp}(-E/RT).$$

R. Capart [19] quoting Fairbridge et al. [20] and Hajaligol et al. [21], gives another equation of the kinetics of decomposition in the form of an equation of Avrami–Erofeev type applicable to materials whose porosity changes during the reaction:

$$\ln(1-\alpha)^n = -k \cdot t. \tag{9}$$

The experimental data allow, by a judicious exploitation of Eq. (8), the determination of α, the order *n*; the pre-exponential factor Ko, the energy of activation *E*, and the kinetic constant *K* which follows the law of Arrhenius.

The order *n*, in the majority of works, has a value ranging between zero and one (Table 11).

K, Ko, *E* and *n* starting from experimental results, will be determined by assuming that pyrolysis process is a first-order reaction.

This work will be focused on the mass loss of the biomass according to the temperature (*T*) and the residence time (ts) during the pyrolysis process.

Let *f* be the fraction of maritime pine not converted to charcoal at time ts

$$f(T) = 1 - m(T,\mathrm{ts})/m(T,0). \tag{10}$$

The loss of mass is expressed by the law of first order:

$$\mathrm{d}m(T,t)/\mathrm{d}t = -K \cdot m(T,t). \tag{11}$$

Eqs. (8) and (10) gives $K \cdot m = m_0$ (d*f*/dt) which gives:

$$\ln(f/\mathrm{fo}) = -K \cdot \mathrm{ts} \tag{12}$$

with fo=*f* (*T*, 0).

Table 10 – Values of kinetic constants *K*

Temperature (°C)	K (s^{-1})	R^2: correlation coefficients
550	$4 \cdot 10^{-6}$	0.9699
650	10^{-5}	0.9968
750	$2 \cdot 10^{-5}$	0.9984

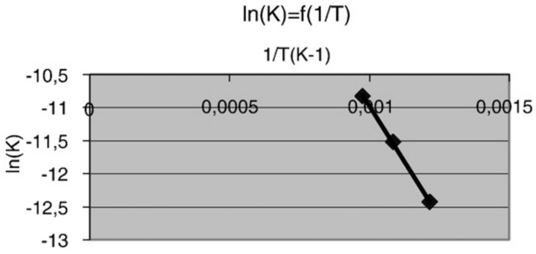

Fig. 7 – Determination of the energy of activation and the exponential pre-factor: curve, ln (*K*)=*f* (1/*T*): Graphically one gets: Y=−6782.5(1/*T*)−4.1807 $R^2=0.9997$.

Another expression of Eq. (11) is the following:

$$\ln[(m(T,0) - m(T,\mathrm{ts}))/m(T,0)] = -K \cdot \mathrm{ts}. \tag{13}$$

Eqs. (12) or (13) shows that the curve [ln (*f*)=*f* (ts)] is a straight line whose slope is (−*K*).

The preceding equations make it possible to determine the energy of activation *E* and the pre-exponential factor Ko starting from the experimental results obtained for a biomass flow (m_0) of 15 kg/h, the outgoing flow (*m*) being that of charcoal.

Curves of Fig. 6 are lines whose slopes make it possible to determine the kinetic constants *K* (Table 10).From *K*=Ko·Exp (−*E*/RT) one gets ln (*K*)=ln (Ko)−*E*/(RT).

The curve ln (*K*)=*f* (1/T) is represented on Fig. 7.

One gets: ln (*K*)=−6782.5 (1/*T*)−4.1807 with a very good coefficient of correlation $R^2=0.9997$. The deduction gives:

- *E*/*R*=6782.5 K from where *E*=56.36 KJ/mol
- the pre-exponential factor Ko=$15.29 \cdot 10^{-3}$ s^{-1}.

The value of the energy of activation is very close to the value 60.73 kJ/mol found by Fofana [22] for temperature varying from 550 °C to 800 °C. On the other hand the pre-exponential factor diverges; he finds 16.84 s^{-1} for wood and its experimental device was a pyrolysor with a vibrating bed [22]. These divergences can be explained by the operating conditions and the size of the particles because these kinetic factors strongly depend on the experimental techniques (T.G.A or other devices used) and vary enormously in the literature [19,23]. It should be noted that, in spite of a high flow of biomass (15 kg/h), the results obtained with this experimental set-up are in agreement with those met in the literature where the experimental flows are very low (less or around 1 kg/h) and where the mass of the samples is weak (a few grams) while the experimental technique usually used is TGA [1,19]. In this study, the results obtained with very good coefficients of correlation; show that the reaction of pyrolysis follows a law of Arrhenius of first order.

In Table 11, some values of Ko, *E*, *n* recorded in the literature are gathered. They illustrate the variation of these constants according to the experimental techniques and the range of the temperatures used.

4. Conclusions

The pyrolysis of maritime pine wood (*P. pinaster* delivered from Ardeche (France)) was carried out on a new two-stage

Table 11 – Kinetic constants of the pyrolysis of the biomass published by researchers [19]

Type of biomass	Experimental technique	Temperature (°C)	Ko (s^{-1})	E (KJ/mol)	*n*	Reference
Wood (sawdust)	TGA (vacuum)	280–325	$3.22\cdot10^{5}$	96.1	0	Tang and Neil [24]
		325–350	$6.5\cdot10^{16}$	226.0	1	
Cellulose		240–308	$6.4\cdot10^{9}$	146.3	0	
		308–360	$3.95\cdot10^{17}$	234.5	1	
Lignin		280–344	$1.64\cdot10^{4}$	87.8	0	
		344–435	0.93	37.5	1	
Beech (pieces)	TGA (N_2)	20–275	$4.33\cdot10^{7}$	104.5	1	Roberts [25]
		20–435	$1.5\cdot10^{3}$	62.7	1	
Pine Douglas	TGA (air)	110–220	$1.9\cdot10^{9}$	104.5	1	Stamm [26]
Cellulose		110–220	$4.8\cdot10^{9}$	108.7	1	
Hemicellulose		110–220	$3.6\cdot10^{10}$	111.6	1	
Lignin		110–220	$1.4\cdot10^{10}$	96.1	1	
Resinous		94–250	$5.1\cdot10^{9}$	123.3	1	
	Bath metal.	167–300	$2.3\cdot10^{11}$	124.5	1	
Filter paper	–	165–265	$7.5\cdot10^{11}$	129.6	1	Kujirai and Akahira [27]
Cellulose	TGA (N_2)	250–330	$1.8\cdot10^{16}$	224.0	1	Akita and Kase [28]
Filter paper	TGA (vacuum, He)	<1000	$6.78\cdot10^{9}$	139.6	1	Lewellen et al. [29]
Spruce						
<54% Conv	TGA	250–450	$2.66\cdot10^{18}$	217.3	–	Leu [30]
>54% Conv			$1.22\cdot10^{16}$	217.3		
Poplar (sawdust)	Fluidized bed	180–330	0.053	18.0	1	Baroah and Lon [31]
			$1.07\cdot10^{1}$	17.0	2	
		330–400	$2.33\cdot10^{4}$	84.0	1	
			$4.0\cdot10^{9}$	114.9	2	
Cellulose	TGA (N_2)	250–450	$6.07\cdot10^{9}$	153.0	0.46	Antal et al. [32]
Birch (sawdust)	TGA (N_2)	200–900	1.7	45.1	0.5	Fong and Ross [33]
Maple (pieces)	TGA	107–150	$1.2\cdot10^{10}$	138.3	1	M^c Naughton [34]
Cellulose	Gasometry	300–1100	$3.33\cdot10^{6}$	132.8	–	Hajaligol [21]
Pine (pieces)	TGA (N_2)	400–1200	1.29	4.18	1	Maa [35]
			$9.9\cdot10^{31}$	445.2	1	
Oak (sawdust)	Gasometry (N_2)	300–400	$2.46\cdot10^{6}$	106.6	1	Thurner
Wood (granulometry: 3–12 mm)	Furnace vibro-fluidized (vacuum)	550–800	16.84	60.73	1	Fofana A [22]
Bark of pine (5–9 mm)			11.44	62.91	1	
Straw (1–6 mm)			$7.59\cdot10^{-3}$	7.09	1	
Rice straw (3–5 mm)			$7.36\cdot10^{-3}$	7.19	1	
Moroccan *Eucalyptus* (<2 mm, 5 mg)	TGA (N_2) dynamic	220–300	$9.43\cdot10^{9}$	130.17	1	F. Kifani-Sahban et al. [23]
		300–360	$3.22\cdot10^{17}$	226.72	1	
Maritime pine (5–30 mm, 15 kg/h)	Pyrolysor with screw (vacuum)	550–750	$15.29\cdot10^{-3}$	56.36	1	This work

TGA: Thermogravimetric Analysis.
(N_2): under nitrogen.

gasifier recently installed on CIRAD facilities in Montpellier. The pyrolysis of this biomass leads to solid, liquid and gaseous phases whose production strongly depends on temperature but also on residence time and weakly on the biomass flow rate in the experimental conditions.

The characteristics of the charcoal (solid phase) established by proximate analysis and the ratio of the charcoal to the raw biomass vary in the following way:

- an increase in temperature reduces charcoal yield and that of VM, but increases FC rate. Ashes rate varies very slowly with temperature according to the experimental parameters studied.
- quality and quantity of charcoal evolve in contrary direction with temperature. Temperature effect on charcoal production is more remarkable than those of biomass flow rate and residence time.

On the other hand, increasing residence time, improves charcoal quality by increasing FC, reducing VM whereas ashes rate variation is slightly appreciable.

The pyrolysis useful gases obtained are H_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6 whose production increases with the rise of temperature.

Increasing residence time leads to the increase of H_2, CH_4, CO_2 and the decrease of CO, while C_2H_2 and C_2H_6 vary very slightly. These results can be explained by the appearance of some reactions such as the methanation and the gasification of the carbon whose importance increases with the rise of temperature.

The liquid phase contains a lot of components which belong to different families of tars.

Low temperatures (450 °C and 550 °C) promote the production of primary and secondary tar classes like furfurals, sugar, methoxyphenols and phenolics. On the other hand, the high temperatures (650 °C and 750 °C) promote the production of heavy and stable molecules (classes three and four) which belong to benzene and aromatics families such as benzene, toluene, naphthalene.

Increasing residence time promotes the cracking of tars.

Low pyrolysis temperatures lead to a great quantity of liquids while high temperatures reduce their production.

The energy evaluation on pyrolysis charcoal and gases shows that the high heating value of gases increases with the rise of temperature but for charcoal its highest value: 33.64 MJ/kg is obtained at 650 °C and decreases after.

The sum of the higher calorific values of charcoal and the gas (charcoal+gas) increases with the increase of the temperature. The gas obtained in the pyrolysis conditions is comparable to gases with average calorific value since its high calorific values vary from 7 to 16 MJ/Nm^3.

According to French standards, charcoal obtained at higher temperatures belongs to class A and it can be used for industrial applications.

The kinetics of charcoal generation during the pyrolysis process is a first-order reaction according to the experimental conditions: so activation energy calculated is 56.36 kJ/mol and the pre-exponential factor is $15.29 \cdot 10^{-3}$ s^{-1}.

The convenient experimental conditions to obtain the most favorable pyrolysis of *Pinus pinaster* from Ardeche from an energetic point of view should be:

- temperature between 650 °C and 750 °C
- residence time: 30 min
- biomass flow rate: 10 or 15 kg/h.

In these conditions, charcoal produced has a higher heating value of about 33 MJ/kg and a rate of FC more than 90% which allows its use in industrial applications. Liquids and gases generated have an acceptable yield and the higher heating value of gases is approximately 15 MJ/Nm^3 which allows classifying them among the gases with average calorific value.

Acknowledgements

The research is partly funded by the European commission in the framework of 6th programme, the ADEME and AUF (Agence Universitaire de la Francophonie).

This work is being carried out by the following main partners: CIRAD, TKEnergi A.S, DTU, and CEA.

REFERENCES

[1] J.M. Encinar, J.F. Gonzalez, J. Gonzalez, Fixed-bed pyrolysis of *Cynara cardunculus* L. Product yields and compositions, Fuel Processing Technology 68 (2000) 209–222.
[2] W.F. Fassinou, L. Van de Steene, E. Martin, F. Broust, J.S. Teglbbjaerg, H.L. Pham, Char quality and tar formation interdependence: first experiments in a new two-stage gasifier, proceedings of 14th European Biomass Conference, Paris, 2005, pp. 620–623.
[3] Association Française de Normalisation, charbon de bois et briquettes de charbon à usage domestique: dénomination, spécifications, essais. AFNOR 84361 NF B 55-101, (20 September 1984).
[4] S.V.B. van Paasen, J.H.A. Kiel, J.P.A. Neeft, H.A.M. Knoef, G.J. Buffinga, U. Zielke, et al., Guideline for sampling and analysis of tar and particles in biomass producer gases — final report documenting the guideline, R&D work and dissemination, Report ECN-C-02-090, ECN, Petten, the Netherlands, 2002.
[5] The Guideline (version 3.3) can be downloaded at the web-site www.tarweb.net.
[6] W.R. Chang, M. Kelbon, B. Krieger-Brockett, Single-particle biomass pyrolysis: correlations of reaction products with process conditions, Industrial and Engineering Chemistry Research 27 (1968) 2261–2275.
[7] J.M. Encinar, F.J. Beltran, A. Bernalte, A. Ramiro, J.F. Gonzàlez, Pyrolysis of two agricultural residues: olive and grape bagasse. Influence of particle size and temperature, Biomass and Bioenergy 11 (1996) 397–409.
[8] M.J. Antal Jr., M. Gnonli, in: A.V. Bridgwater (Ed.), Fundamental of Charcoal Production in Fast Pyrolysis of Biomass: A Handbook. Vol. 3, 2005, pp. 149–160.
[9] J.M. Encinar, F.J. Beltran, A. Bernalte, A. Ramiro, J.F. Gonzàlez, Pyrolysis, of two agricultural residues: olive and grape bagasse. Influence of particle size and temperature, Biomass and Bioenergy 11 (1996) 397–409.
[10] F. Shadizadeh, Advances in Carbohydrate Chemistry 23 (1968) 419.
[11] P. Morf, P. Hasler, T. Nussbaumer, Mechanisms and kinetics of homogenous secondary reactions of tar from continuous pyrolysis of wood chips, Fuel 81 (2002) 843–853.
[12] J. Fjellenip, J. Ahrensfeldt, B. Gobel, U. Henriksen, Formation, Decomposition and Cracking of Biomass Tars in Gasification, Biomass gasification Group, Department of mechanical engineering, The Technical University of Denmark (DTU), 2005, p. 12, 5.
[13] T.A. Milne, N. Abatzoglou, R.J. Evans, Biomass Gasifier Tars: Their Nature, Formation and Conversion, *US* department of Energy, 1998.
[14] P. Rousset, Modification des constituants du bois sous l'effet de la chaleur et conséquences sur ses propriétés in Formation à la valorisation énergétique de la biomasse lignocellulosique. Edition: Cirad, 1997, pp. 171–187.
[15] H. Egsgaard, E. Larsen, Proceedings of the First World Conference and Exhibition on Biomass for Energy Industry, Sevila, June 2000, pp. 1468–1471.
[16] M. Frenklach, H. Wang, H. Bockhorn (Eds.), Soot Formation in Combustion — Mechanisms and Models, Springer, Berlin, 1994.
[17] Ph. Hasler, R. Bühler, Th. Nussbaumer, Evaluation of Gas Cleaning Technologies for Small Scale Biomass Gasifiers, Swiss Federal Office of Energy and Swiss Federal Office for Education and Science, 1997.
[18] P. Corté, F. Pinta, La gazéification: aspects théoriques et technologie mise en œuvre, in: P. Girard, P. Rousset (Eds.), Formation à la valorisation énergétique de la biomasse lignocellulosique, Edition: Cirad, 1997, p. 272.
[19] R. CAPART, La gazéification du bois. Etude expérimentale et théorique de la pyrolyse du bois brut et des réactions d'oxydation du charbon de bois avec le dioxyde de carbone et la vapeur d'eau, Thèse de l'université de technologie de Compiègne (1991) PP18, 19, 23, 41–42, 114.
[20] C. Fairbridge, R.A. Ross, S.P. Sood, A kinetic and surface study of the thermal de composition of the cellulose powder in inert and oxidizing atmospheres, Journal of Applied Polymer Science 22 (1978) 497.
[21] M.R. Hajaligol, W.A. Peters, J.B. Howard, J.P. Longwell, Product compositions and kinetics for rapid pyrolysis of cellulose, Industrial & Engineering Chemistry Process Design and Development 21 (1982) 457.
[22] A. Fofana, Traitement pyrolytique de résidus en four vibrofluidisé: application à la biomasse et aux boues de station d'épuration, Thèse de l'Université de technologie de Compiègne, 2003, PP.96.

[23] F. Kifani-Sahban, L. Belkbir, A. Zoulalian, Détermination des paramètres cinétiques de la pyrolyse lente de l'Eucalyptus marocain, Thermochimica Acta 289 (1996) 33–40.

[24] W.K. Tang, W.K. Neil, Effects of flame retardants on pyrolysis and combustion of α cellulose, Journal of Polymer Science, Part C (6) (1964) 65.

[25] A.F. Robert, G. Clough, Thermal decomposition of wood in an inert atmosphere, 9th Int. Symp. on Combustion, 1963, p. 158.

[26] A.J. Stamm, Thermal degradation of wood and cellulose, Industrial and Engineering Chemistry 48 (1956) 413.

[27] T. Kujirai, T. Akahira, Scientific papers of the Institute of Physical and Chemical Research, Tokyo 2 (1925) 223.

[28] K. Akita, M. Kase, Determination of kinetic parameters for pyrolysis of cellulose and treated with ammonium phosphate by DTA and TGA, Journal of Polymer Science 15 (1967) 833–848.

[29] P.C. Lewellen, W.A. Peters, J.B. Howard, Cellulose pyrolysis kinetics and char formation mechanism, 16th Symp Int. on Combustion, Combustion Institute, Pittsburgh, 1976, pp. 1471–1480.

[30] J.C. Leu, Modelling of the pyrolysis and ignition of wood, PhD thesis. University of Oklahoma, 1975.

[31] J.N. Baroah, V. D Lon, Rates of thermal decomposition of some carbonaceous materials in a fluidized bed, Fuel 55 (1980) 141.

[32] M.J. Antal, H.L. Friedman, F.E. Rogers, kinetics of cellulose pyrolysis in N_2 and steam, Combustion of Science Technology 21 (1980) 141.

[33] P. Fong, R.A. Ross, Pyrolysis of white birch in N2 and He up to 900 °C in the presence of water vapour zinc–chromite and iron oxide, Wood Science 13 (1980) 87.

[34] G.C. Mc Naughton, Ignition charring temperature of wood, Wood Products 50 (2) (1979) 21.

[35] P. Maa, Influence of particle size and environmental conditions on high temperature pyrolysis of the cellulose material, PhD Thesis. West Virginia University, 1971.